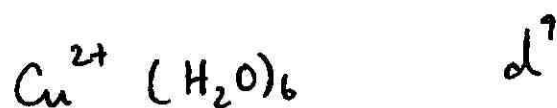
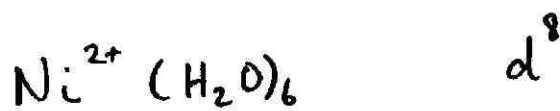
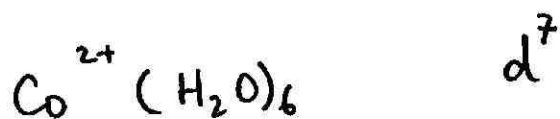
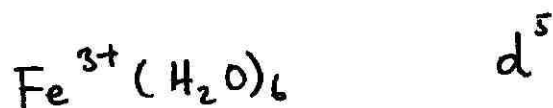
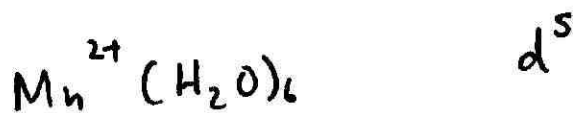
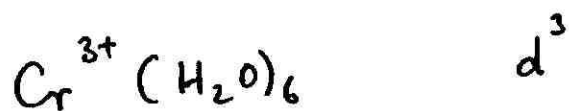
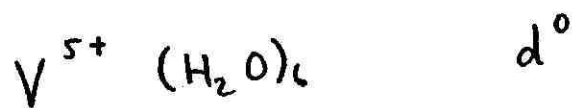
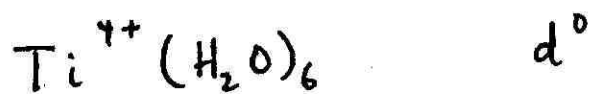
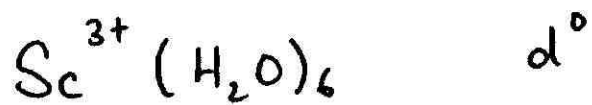


③ In transition metal complexes all kinds of d^n (n variable) exist. Let's consider the common ions in water:

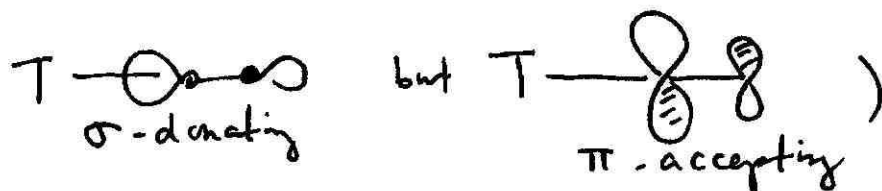


Other oxidation states are also often found:

Fe^{2+} , Co^{3+} & Cu^+ are three of the most common. Also in complexes with CO the 0 oxidation state is often zero.

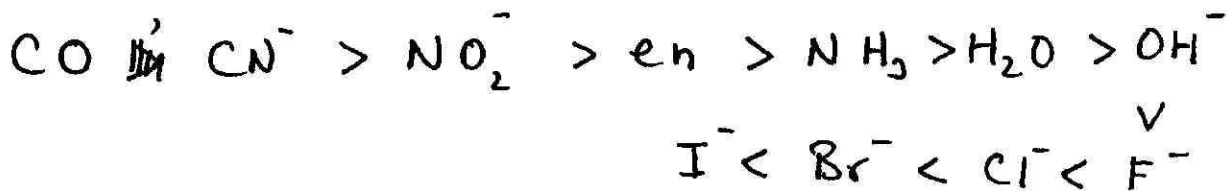
④ Ligands such as NH_3 act only as HOMO's and are called $\sigma(e^-)$ donors (The $\text{T}-\text{NH}_3$ involves a sigma interaction $\text{T}-\text{N}(\text{H})_3$).

Ligands such as $\text{C}\equiv\text{O}$ act not only w/ HOMO's but also LUMO's. They are called σ -donors and π -acceptors. (The e^- donating HOMO is a σ orbital, the e^- accepting LUMO is a π -orbital):



⑤ π acceptors make large ΔE ($t_{2g}-e_g$ gap). Pure σ donors make small ΔE gaps.

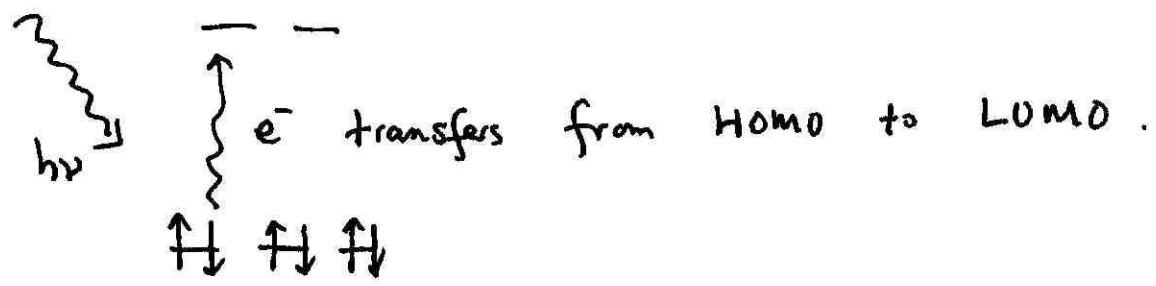
This is summarized in the spectrochemical series.



CO, CN^- are π acceptors.

$\text{NH}_3, \text{H}_2\text{O}$ and halides are σ -donors.

⑥ The size of ΔE affects the physical properties two ways. It affects the color of the compound and it affects the magnetism.



If the molecule absorbs high energy light then the color will be dominated by low energy light.
 If the molecule absorbs low energy light then the color will be dominated by high energy light.

	Color of light absorbed	color of light observed	
high energy color	{ violet blue blue-green	greenish yellow	} low energy color
		yellow	
		red	
low energy color	{ yellow-green yellow orange red	violet	} high energy color
		dark blue	
		blue	
		green	

⑧ We can examine the series of Cr^{3+} compounds

	color	light absorbed	ΔE
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	violet	yellow-green	largest

$\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$	blue-green	orange-red	intermediate
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$\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$	green	red	smallest
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& Cl^- has a smaller ΔE affect than H_2O as H_2O is stronger on the spectrochemical series.

Similarly we can examine:

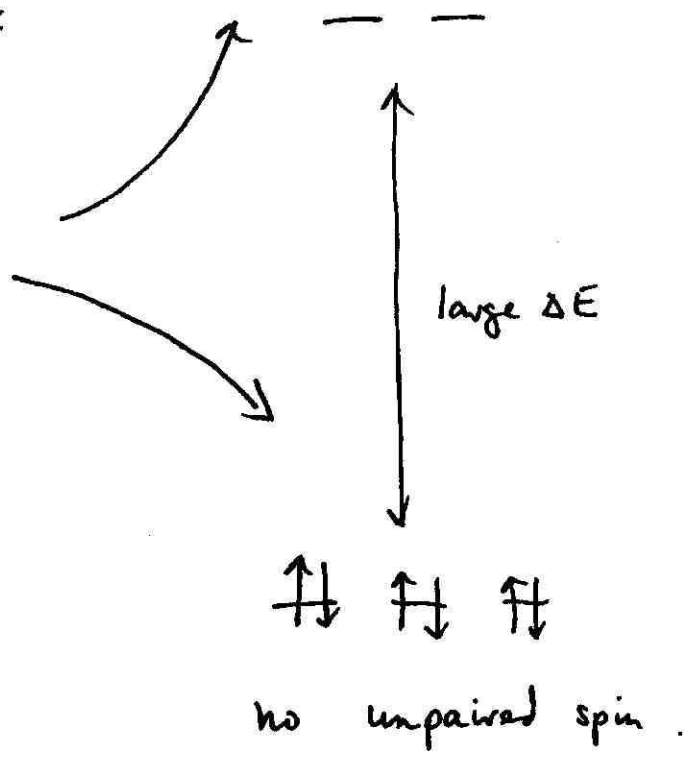
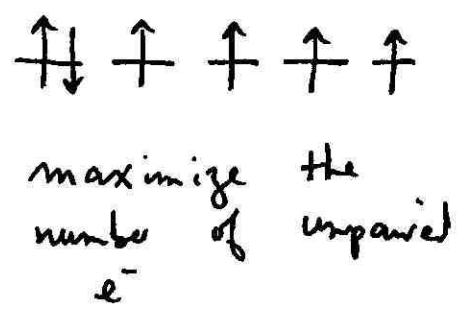
	color	light absorbed	ΔE
$\text{Cr}(\text{NH}_3)_6^{3+}$	yellow	blue	large

$\text{Cr}(\text{NH}_3)_4\text{Cl}_2^+$	violet	yellow-green	small
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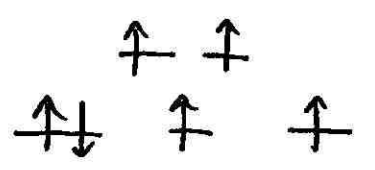
Note the ΔE splitting is $\text{Cr}(\text{NH}_3)_6^{3+}$ is larger than $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. Why is that?

⑨ The 2nd physical effect of the spectrochemical series is in the magnetism of the compound.

⑩ Review Hund's rules:



⑪ What about a very small ΔE ?

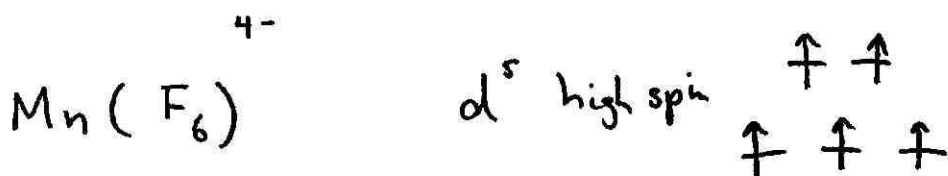
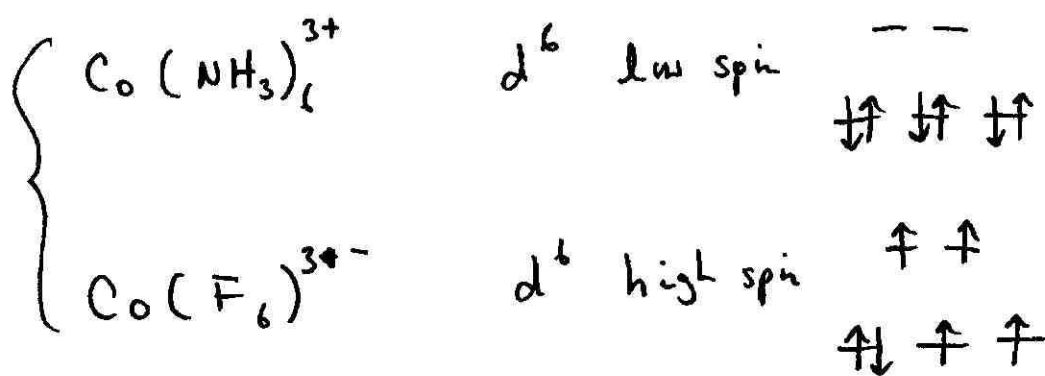
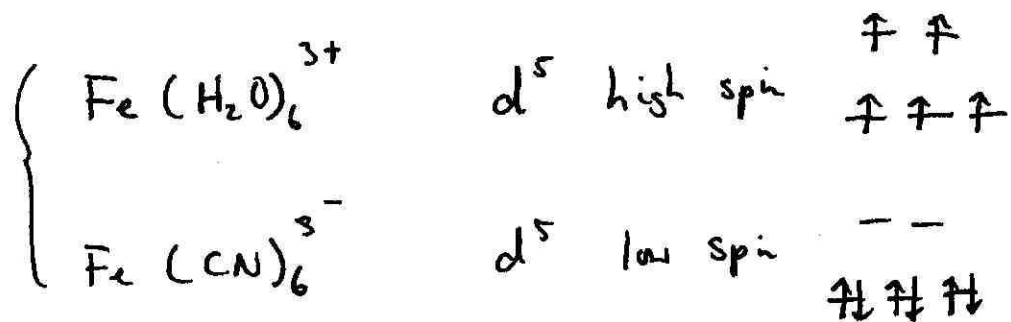


Hund's rule will still be obeyed.

⑫ Ligands with large ΔE always occupy the lowest energy orbitals. So CO and CN⁻ are low-spin ligands.

Metal ions in +2 oxidation state w/ ligand like H₂O or halide have small ΔE . They obey Hund's rule for d-orbitals. These are high-spin systems.

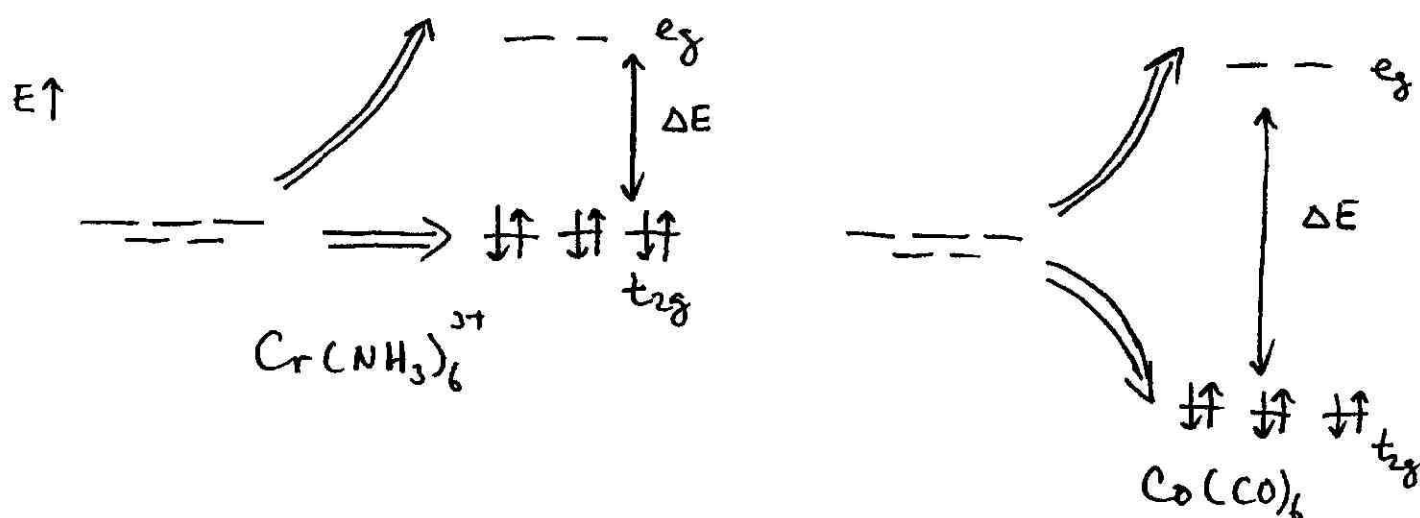
For $+3$ ions the situation is mixed.



Lecture 38 High spin, low spin, π acceptors & σ donors.

① This will be the last lecture on inorganic MO theory. Our goal will be to put together the two previous lectures and to connect them to experimental data.

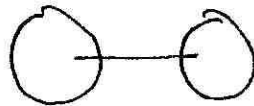
② Summary of last 2 lectures. Looking only at the d-orbital portions of the $\text{Cr}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{CO})_6$ MO diagrams:



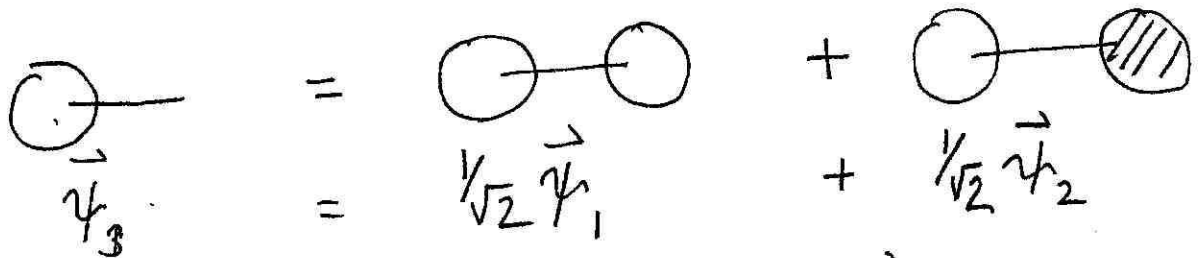
ΔE is large for $\text{Co}(\text{CO})_6$. For $\text{Cr}(\text{NH}_3)_6^{3+}$ ΔE is small.

Example: H_2

two energy eigenstates: $\vec{\psi}_2$  —

$\vec{\psi}_1$  —

Any state can be expressed as a combo of the eigenstates.

$$\vec{\psi}_3 = \frac{1}{\sqrt{2}} \vec{\psi}_1 + \frac{1}{\sqrt{2}} \vec{\psi}_2$$


\therefore P.A. $\vec{\psi}_3$ behaves as $\vec{\psi}_1 = 1/\sqrt{2}$
 " " " " $\vec{\psi}_2 = 1/\sqrt{2}$

eg.  accepts $h\nu$ $1/2$ as much as 

